

PATENT SPECIFICATION

(11) 1249 668

1249 668

NO DRAWINGS

- (21) Application No. 61453/68 (22) Filed 24 Dec. 1968
 (31) Convention Application No. 84844 (32) Filed 29 Dec. 1967 in
 (33) Japan (JA)
 (45) Complete Specification published 13 Oct. 1971
 (51) International Classification C 08 f 1/00 3/16 C 07 f 1/02,
 C 08 f 25/00
 (52) Index at acceptance
 C3P 12D1 12DX 12P1 13D1A 13D1B 13G4A 13G5
 13H3 13N4 13R2B 13T1B 13Y
 C2J 7A 7Y



(54) IMPROVEMENTS IN THE POLYMERISATION OF CONJUGATED DIENES

(71) We, JAPAN GAS-CHEMICAL COMPANY INC., a Japanese Body Corporate of 1—1, 2-chome, Uchisaiwai-cho, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the manufacture of a lithium-hydrocarbon adduct and of polymers of conjugated dienes by polymerising conjugated dienes in the presence of a catalytic amount of the lithium-hydrocarbon adduct. In particular this invention relates to the manufacture of polymers of conjugated dienes having a high cis-1,4 structural unit content and excellent mechanical properties using, as initiator, an oligomeric dilithium adduct (i.e. oligomer dilithium) having a substantially uniform molecular weight.

It is known that a complex formed between a polycyclic aromatic hydrocarbon and an alkali metal is capable of initiating the polymerisation of various anionic monomers. For instance, U.S. Patent Specification No. 3,170,903 discloses a process for polymerising isoprene or butadiene using a complex of lithium and a polycyclic aromatic hydrocarbon such as naphthalene. Such a complex is not sufficiently soluble in a non-polar solvent, and therefore it is difficult to control the molecular weight of the resulting polymer. Consequently, the molecular weight distribution of the resulting polymer tends to be broad. This method has the further disadvantage that the cis-1,4 structural unit content of the conjugated diene polymer obtained is not sufficiently high, with the result that when such conjugated diene polymers are made into vulcanized rubber products, the products have inferior mechanical properties such as modulus, elongation and tensile strength.

U.S. Patent Specification Nos. 3,157,604 and 3,287,333 disclose the preparation of a polymerisation initiator by reacting lithium with isoprene, butadiene or styrene in the presence of a polycyclic aromatic compound, and the polymerization of a conjugated diene, alone, or with a vinyl-substituted aromatic hydrocarbon, using this polymerisation initiator to form a homopolymer or a block copolymer. According to this method of producing a polymerisation initiator, however, the molecular weight distribution of the lithium oligomer adduct obtained is very broad and contains as by-products, a product of 1,2- or 3,4-structural units having a low degree of polymerisation and simultaneously a product of 1,2- or 3,4-structural units having a high degree of polymerisation. Thus the reaction product becomes very viscous, and it is difficult to remove therefrom the polar solvent, e.g. an ether used, and this solvent adversely affects the 1,4-polymerisation of conjugated dienes. In addition a small amount of complex of lithium and polycyclic aromatic hydrocarbon or metallic lithium still remains in the reaction product, and thus it is difficult to obtain a homogeneous solution of the initiator. This in turn makes it difficult to control the molecular weight of the conjugated diene polymers obtained. Thus employing this method, it is difficult to obtain polymers of conjugated dienes which contain more than 90% cis-1,4 structural units and whose molecular weight distribution is controlled within a narrow range. Furthermore, when made into rubber products by compounding and vulcanizing, these polymers have only low mechanical properties.

We have found that when metallic lithium is reacted with a polycyclic aromatic hydrocarbon in an aliphatic ether, insoluble residues are removed from the reaction product, and a conjugated diene hydrocarbon or vinyl

or vinylidene-substituted aromatic hydrocarbon is added to the solution obtained, it is possible to control the molecular weight distribution of the oligomeric lithium hydrocarbon adduct obtained in the reaction product within a very narrow range, and the aliphatic ether in the reaction product can be removed with ease and completeness. It has also been found that the reaction product after removal of substantially all the aliphatic ether, readily dissolves in a non-polar solvent, such as an aromatic or aliphatic hydrocarbon to form a homogeneous solution of polymerisation initiator; that when the polymerisation of conjugated dienes is conducted using this polymerisation initiator solution, the molecular weight distribution of the polymers obtained can be controlled within a narrow range and the cis-1,4 structural unit content of the polymer can be maintained at a high level; and that vulcanized rubber products obtained from the so produced conjugated diene polymers have excellent mechanical properties such as tensile strength, rubber elasticity, rigidity, tear strength, abrasion resistance and flexural strength.

The invention provides a process for preparing a lithium-hydrocarbon adduct which process comprises i) reacting, in the presence, as solvent, of an aliphatic ether, metallic lithium with a polycyclic aromatic hydrocarbon having 10 to 30 carbon atoms, ii) removing insoluble material from the reaction product of i), iii) adding to the solution obtained from ii) 1 to 10 moles, per gram atom of lithium in the solution, of a conjugated diene hydrocarbon or a vinyl or vinylidene-substituted aromatic hydrocarbon; and then iv) substantially removing all the aliphatic ether from the resulting solution. The present invention also provides a process for polymerizing an anion-polymerisable conjugated diene hydrocarbon in a non-polar solvent in the presence of the lithium-hydrocarbon adduct prepared as described above.

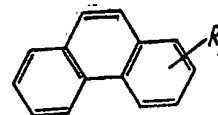
The polycyclic aromatic hydrocarbons to be used in the process of the invention are hydrocarbons which are not anion-polymerisable and contain 10—30, preferably 10—20, carbon atoms and 2—5, preferably 2—3, aromatic rings. Specific examples of such polycyclic aromatic hydrocarbons are:

Hydrocarbons of the naphthalene series of the formula:

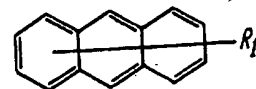


wherein each of R_1 and R_2 , which may be the same or different, represents a hydrogen

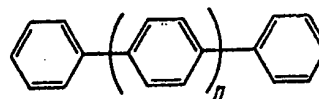
atom or an alkyl group of 1—4 carbon atoms, such as naphthalene, 1-methyl naphthalene, 2-methyl naphthalene, 1-ethyl naphthalene and 2-propyl naphthalene; hydrocarbons of the phenanthrene series of the formula



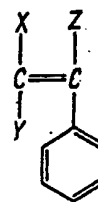
wherein R_1 is a hydrogen atom or an alkyl group having 1—4 carbon atoms, such as phenanthrene, 2-methyl phenanthrene, and 4-ethyl phenanthrene; hydrocarbons of the anthracene series of the formula



wherein R_1 is a hydrogen atom or an alkyl group having 1—4 carbon atoms, such as anthracene, 1-methyl anthracene, and 2-ethyl anthracene; polyphenyls of the formula



wherein n is 0 or an integer of 1 to 3, such as diphenyl and terphenyl; and aromatic compounds of the formula:

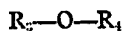


wherein each of X , Y and Z , which may be the same or different is a hydrogen atom, or a phenyl group, with the proviso that at least one of X , Y and Z is a phenyl group, such as stilbene, triphenyl ethylene and tetraphenyl ethylene.

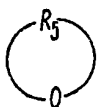
Especially preferable polycyclic aromatic hydrocarbons are naphthalene, phenanthrene and diphenyl.

In the production of the polymerisation initiator according to this invention, metallic lithium is generally reacted with the polycyclic aromatic hydrocarbon in an aliphatic ether in an inert atmosphere. The ratio of the metallic lithium (Li) to the polycyclic aromatic hydrocarbon (Ar) may be varied within a wide range, but a molar ratio of Li:Ar of 1:0.1 to 1:10 is advantageous in handling these materials. The reaction (i) of lithium with polycyclic aromatic hydrocarbon may generally be carried out at a temperature of -80° to 50°C . The reaction time differs according to the temperature, but in general, a reaction time of 1—48 hours is sufficient. The completion of the reaction can be confirmed by measuring the lithium content (excluding untreated lithium) in an aliphatic ether solution of the reaction mixture.

The aliphatic ethers usable in the present process include chain or cyclic aliphatic monoethers, examples of which are ethers represented by the formulae



wherein each of R_3 and R_4 , which may be the same or different, represents an alkyl group having 1—4 carbon atoms, the sum of the carbon atoms of R_3 and R_4 being at least 3; and



wherein R_5 is a straight-chain alkylene group having 4 or 5 carbon atoms.

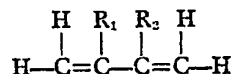
Preferred aliphatic ethers are diethylether and tetrahydrofuran, but diisopropyl ether, di-n-butyl ether, methyl ethyl ether, ethyl-n-propyl ether and tetrahydropyran can of course be used. The ratio of the aliphatic ether to the polycyclic aromatic hydrocarbon can be varied within a wide range, but it is preferable to use 1—20 litres of the aliphatic ether per mole of the polycyclic aromatic hydrocarbon. The use of less aliphatic ether gives a viscous reaction product. The use of a larger amount is not preferable from the economical point of view.

In step ii) insoluble material is removed from the reaction mixture obtained from step i) by such procedure as filtration, centrifugal separation and decantation. The removal of the insoluble material is of the utmost importance in the present invention. The insoluble material comprises excess or unreacted metallic lithium. Reaction of the adduct of lithium and the polycyclic aromatic hydrocarbon with a conjugated diene, vinyl- or

vinylidene-substituted aromatic hydrocarbon in the presence of this metallic lithium would not give a polymerisation initiator having a uniform molecular weight distribution. Furthermore, the initiator solution thus obtained would give a slurry, when the polar ether solvent of the initiator solution was replaced by a non-polar solvent.

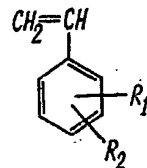
The solution obtained after removal of the insoluble residue, is an aliphatic ether solution of an adduct of the polycyclic aromatic hydrocarbon and lithium. To this solution is added an ethylenically unsaturated hydrocarbon which is a conjugated diene hydrocarbon, vinyl- or vinylidene-substituted aromatic hydrocarbon in an amount of 1—10 moles, preferably 1—5 moles, per gram-atom of the lithium in the solution thereby to cause the added hydrocarbon and the adduct to react.

The conjugated diene hydrocarbons used in this step (iii) may be of the formula:



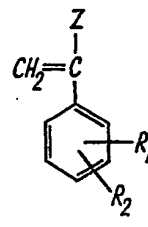
wherein each of R_1 and R_2 , which may be the same or different, represents a hydrogen atom or an alkyl group having 1—4 carbon atoms such as butadiene, isoprene, 2,3 - dimethyl - 1,3 - butadiene, 2 - ethyl - 1,3 - butadiene and 2,3 - diethyl - 1,3 - butadiene. 1-phenylbutadiene may also be used.

The vinyl-substituted aromatic hydrocarbons are styrene derivatives which may be of the formula:



wherein each of R_1 and R_2 , which may be the same or different, is a hydrogen atom or an alkyl group having 1—4 carbon atoms such as styrene, o, m, and p-methyl styrenes.

As the vinylidene-substituted aromatic hydrocarbons, there can be mentioned α -alkyl styrene derivatives of the formula



wherein each of R_1 and R_2 , which may be

the same or different, represents a hydrogen atom or an alkyl group having 1-4 carbon atoms, and Z is an alkyl group having 1-4 carbon atoms, such as α -methyl styrene and α -methyl-o, m or p-methylstyrene.

The reaction of an adduct of lithium and the polycyclic aromatic hydrocarbon with the anion-polymerisable ethylenically unsaturated hydrocarbon is exothermic, and it is preferable to conduct the reaction by adding the ethylenically unsaturated hydrocarbon, while agitating, to a solution of the adduct. Generally, it is preferred that this reaction should be conducted at a temperature of -80° to 50°C . for a period of 30 minutes to 2 hours. The completion of the reaction can be easily confirmed by the colour of the reaction mixture; for instance, the naphthalene lithium adduct is coloured green in its tetrahydrofuran solution, and violet in its diethyl ether solution but the solution turns orange red when oligoisoprenyl dilithium is formed, and red when oligostyryl dilithium is formed. Thus a homogeneous solution of the polymerisation initiator having an active group at each end and preferably containing 2-20 polymerised units derived from the ethylenically unsaturated hydrocarbon used, is obtained.

The aliphatic ether in the reaction product is then substantially all removed.

In order to obtain a diene polymer having a high cis-1,4 structural unit content, it is preferable that the amount of the remaining aliphatic ether should be less than 0.1% by weight, preferably less than 0.05% by weight, and that when it is made into a solution of a non-polar solvent the lithium concentration is 1 gm. atom of lithium/liter of solution. The removal of the aliphatic ether from the reaction product is generally effected by distillation, adding a non-polar solvent, and repeating the distillation to remove further ether. Non-polar solvents which may be used in the polymerisation process include aromatic hydrocarbons or chain or cyclic aliphatic hydrocarbons such as benzene, toluene, xylene, pentane, hexane, heptane, cyclopentane, cyclohexane and petroleum ether. The ether is replaced by the non-polar solvents. The replacement is effected preferably by distillation under vacuum, but the ether may also be removed by refluxing the non-polar solvent.

Thus the present invention has made it possible to obtain a polymerisation initiator whose molecular weight distribution is controlled within a narrow range, and which is dissolved in a non-polar solvent.

The polymerisation of the conjugated dienes can be conducted under conditions known *per se* except that a polymerisation initiator obtained by the above-mentioned method is used as a homogeneous solution in the non-polar solvent. The monomers are

polymerised in the non-polar solvent generally in the presence of an inert gas or under a vacuum at a temperature of -80° to 80°C . for a period of 1 to 30 hours. In order to obtain a high cis-1,4 structural unit content in the resulting polymer, it is preferable to adjust the amount of the residual ether solvent present during the polymerisation to less than 0.006 mole per mole of the conjugated diene monomer. The amount of the non-polar solvent is not particularly critical, but the ratio of diene to solvent affects the rate of polymerisation. The amount of the polymerisation initiator is not particularly critical either, but is determined by the desired molecular weight of the polymer.

Butadiene or isoprene can be used as the conjugated diene polymerised by the process of the present invention, isoprene being particularly preferred. It is also possible to manufacture block copolymers of the conjugated diene monomer and containing less than 50%, preferably less than 40%, by weight of units derived from a monoethylenically unsaturated comonomer copolymerisable therewith. The monoethylenically unsaturated comonomer may be polar or non-polar. Examples of such comonomers are styrene, α -methylstyrene, vinyl toluene, vinyl xylene, ethylvinyl benzene, methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate, acrylonitrile and methacrylonitrile.

Thus for example block copolymers comprising alternate blocks of a conjugated diene polymer and of a monoethylenically unsaturated hydrocarbon polymer may be prepared by polymerising alternately (a) the anion-polymerisable conjugated diene in a non-polar solvent in the presence of the lithium-hydrocarbon adduct prepared as described above and (b) an anion-polymerisable monoethylenically unsaturated monomer in an amount such as to provide less than 50% by weight of polymer units derived from (b) in the final polymer. Similarly block copolymers comprising polymer of a monoethylenically unsaturated monomer linked to both ends of a conjugated diene polymer may be prepared by polymerising the diene in a non-polar solvent in the presence of the lithium-hydrocarbon adduct and then polymerising an anion-polymerisable monoethylenically unsaturated monomer in the presence of the polymer chain so formed in an amount such as to provide less than 50% by weight of the polymer units derived therefrom in the final polymer.

When homopolymers of conjugated dienes are produced by the process of the present invention, it is preferable to produce polymers having a molecular weight in the range of 10,000 to 1,000,000 particularly 100,000 to 1,000,000, and when block copolymers are prepared the final copolymers preferably have a molecular weight in the range of 100,000

to 1,000,000. From this point of view, it is generally preferable that the polymerisation initiator should be used in a ratio such that 1/100 to 1/10,000 gm-atom, particularly 0.1 to 1 milligram-atom of lithium is used per mol of monomer.

The polymerisation can be terminated by introducing methanol, water, air or carbon dioxide gas into the polymerisation system.

The block copolymer may for example be manufactured in one of the following ways.

(I) A non-polar anion-polymerisable monoethylenically unsaturated comonomer e.g. styrene or α -methyl styrene, and a conjugated diene may be alternately introduced into the polymerisation system. The order of addition is not critical, and the addition may be made any number of times.

(II) A "living" polymer chain of a conjugated diene homopolymer, or a "living" block copolymer of a conjugated diene with a non-polar monoethylenically unsaturated monomer, such as styrene and α -methyl styrene, can be formed first, and then a polar anion-polymerisable monoethylenically unsaturated monomer, e.g. methyl methacrylate and acrylonitrile may be introduced.

The conditions for the block copolymerisation are almost the same as those employed in the manufacture of homopolymers. In the copolymerisation of the monoethylenically unsaturated monomer, the use of a polar-solvent is for polar monomers because it makes the polymerisation rate higher, but a non-polar solvent or a mixture of a polar solvent and a non-polar solvent may be used. The amount of the solvent used should preferably be more than 25 times that of the monomer used for the production of homopolymer.

Homopolymers of conjugated dienes or block copolymers of conjugated dienes and monoethylenically unsaturated monomers obtained by the process of this invention have a higher cis-1,4 structural unit content than those obtained by conventional methods. In an isoprene polymer more than 90% of the total number of isoprene units may be cis-1,4 units when prepared by the present process. Furthermore, the polymers obtained by the process of the invention when made into vulcanised rubber products have a better tensile strength, modulus, elongation and other mechanical properties than those obtained by conventional methods.

The block copolymers obtained by the present process have excellent rubber elasticity at low temperatures, and block copolymers containing a relatively high number of thermoplastic polymer segments are impact resistant, and can be easily moulded. A further advantage of the block copolymers of the invention is that they have a uniform composition and are not contaminated by a

homopolymer of the copolymerisable component.

The polymers obtained by the process of the invention may be compounded with a rubber anti-oxidant, such as are amine or phenol series compound; a filling reinforcing agent, such as white carbon (an ultrafine, white, powder, silica type reinforcing agent, 88% SiO_2 , density 1.95 to 2.30 g/cc, particle size 0.02—0.5 μ , B.E.T. surface area or 150 m^2/g , pH of a 5% suspension 9.0—10.0) or carbon black, a filler, such as calcium carbonate, talc or calcined clay, a vulcanising agent, such as sulphur, a vulcanisation promoter, such as an organic sulphide; a vulcanisation promoting adjuvant, such as zinc white, a lubricant, such as a fatty acid or a metal salt of a fatty acid, an extender oil such as a naphthenic or aromatic oil; a peptiser or a pigment in accordance with known compositions.

The polymers of the invention either alone or in blends with natural rubber or other synthetic rubber, have a wide field of application as, for instance, tyres, footwear, belts, rolls, anti-vibratile rubbers, packings, bottle stoppers, and nipples for nursing-bottles.

The invention will be further illustrated by the following Examples. Percentage given in the Examples are by weight.

The microstructure of polyisoprene was determined in accordance with the infrared method described in J. L. Binder and H. C. Ransaw, *Anal. Chem.* 29, 1957, p.p. 503—508. The microstructure of polybutadiene was determined in accordance with J. L. Binder, *Anal. Chem.* 26, 1954, page 1877. Incidentally, Q value is a ratio of a weight average molecular weight (M_w) to a number average molecular weight (M_n) determined by gel-permeation chromatography (GPC), the smaller this value, the narrower the molecular distribution.

EXAMPLE 1

(preparation of an initiator solution)

In a dried, egg plant-shaped flask equipped with a magnetic stirrer and a ground cock, 0.01 mol of naphthalene and 0.5 mol of metallic lithium were charged under an atmosphere of high-purity N_2 , and the pressure inside the system was immediately reduced to 10^{-4} mm Hg. Thereafter 100 ml. of diethyl ether, purified and degasified in advance, were charged under atmospheric pressure and the system was stirred at 25°C. for 40 hours. After the unreacted excess metallic lithium had been filtered off, 0.03 mole of purified styrene monomer was charged under subatmospheric pressure and stirred at -20°C. for 2 hours and 25°C. for 3 hours. After the reaction diethyl ether was removed by vacuum distillation and then 100 ml of benzene were added to the residue, the resulting mixture was stirred for about 30

minutes at room temperature and then the benzene was removed by vacuum distillation. This operation was repeated a further twice. Then 100 ml of benzene were added to

5 give an initiator solution.

The alkali metal concentration in the initiator solution was 0.078 g. atoms/liter and the amount of ether therein was less than 0.01% by weight (a value which could not be

10 measured by gas chromatography).

EXAMPLE 3

The reactor used was a three-necked, 1000 ml, pressure-resistant glass container equipped with a magnetic stirring rod, an inlet for an initiator solution and an inlet for a benzene solution of the monomer. After the interior of the reactor had been dried, 20 ml of the initiator solution obtained in Example 1 and 400 ml of benzene were charged in the reactor under an atmosphere of N_2 and, while the mixture was stirred, 200 ml of isoprene was added. Thereafter the reaction was continued at 30°C. for 6 hours. The reaction product was then added to 1 liter of methanol containing 0.3 g. of antioxidant, β -phenyl-naphthylamine to precipitate the polymer. The precipitate was separated and thereafter dried at 50°C. under sub-atmospheric pressure for 48 hours. The results were as follows.

30	Conversion	93%
	Cis-1,4 structure	94%
	3,4 structure	6%
	1,2 structure	trace
	Molecular weight (average)	210,000
35	Q value	1.66

(Q value denotes M_w/M_n by GPC)

Using this polymer, a test piece was prepared by a standard rubber compound method and the following mechanical characteristics were obtained:

40	Recipe:	parts by weight
	Polyisoprene	100
	Zinc stearate	3
45	Sulfur	2
	TMT (vulcanizing accelerator)	1
	BHT (antioxidant)	1
	Stearic acid	1

50 TMT: (tetramethyl thiuram disulfide)
BHT: (2,6-ditertiary butylphenol)

Vulcanizing conditions:
150°C. 8 min. 150 kg/cm²G

Mechanical properties:

55	300% modulus (kg/cm ²)	Tensile strength (kg/cm ²)	Elongation (%)	Hardness (Shore A)
	11.5	112	980	28

EXAMPLE 3

(preparation of an initiator solution)

An initiator solution was prepared as in Example 1. The amounts of each reagent used were as follows.

(1)	{ Phenanthrene	0.004 mole	
	{ Lithium	0.1 mole	
	{ Diethylether	90 ml	
(2)	Styrene	0.010 mole	65
(3)	n-Hexane	3 × 100 ml	

thereafter 100 ml of n-hexane was added to obtain an initiator solution.

The residual amount of ether in the initiator solution obtained was less than 0.01% by weight and the alkali metal concentration of said solution was 0.036 gm-atom/liter.

EXAMPLE 4

Using the same reactor as in Example 2, under an atmosphere of argon, 10 ml of the initiator solution obtained in Example 3 and 92 ml of benzene were charged in the reactor and while the mixture was stirred, 14 ml of isoprene were added. The mixture was then heated at 60°C. for 30 minutes and at 30°C. for 18 hours. Of 116 ml of the produced polymer solution, 23 ml was taken and treated with methanol.

	Conversion	98%	
	Cis-1,4 structure	93.5%	85
	3,4 structure	4.5%	
	1,2 structure	2.0%	
	Molecular weight (average)	69,000	
	Q value	1.85	

EXAMPLE 5

(preparation of an initiator solution)

In a dried, egg plant-shaped flask equipped with a magnetic stirrer and a ground cock, 0.1 mol of naphthalene and 0.5 mol of metallic lithium were charged under the atmosphere of argon. Thereafter, the pressure inside the system was reduced to 10^{-1} mmHg and 100 ml of tetrahydrofuran, purified and degasified in advance, was charged under subatmospheric pressure. Stirring at 25°C was continued for 6 hours. The unreacted excess metallic lithium was filtered off, next 0.4 mole of isoprene monomer was added under sub-atmospheric pressure, and the mixture was stirred at -20°C. for 2 hours and at 25°C. for 3 hours. Tetrahydrofuran was removed by vacuum distillation, the pressure inside the flask was again reduced to 10^{-1} mmHg, thereafter 100 ml of n-heptane were added and the mixture was stirred. Next the added n-heptane was removed by vacuum distillation, 100 ml of n-heptane were added anew, and the mixture was stirred for 1 hour. Thereafter said n-heptane was completely removed and 100 ml of n-heptane were added anew and

the mixture was stirred for 1 hour. An appropriate amount of said mixture was taken and used as a polymerization initiator.

- 5 The concentration of the alkali metal in the initiator solution obtained was 0.85 gm-atoms/liter as measured by titration with hydrochloric acid. The amount of tetrahydrofuran in the initiator solution was less than 0.01% by weight (a value which could not be measured by gas chromatography).

EXAMPLE 6

- 15 A 150 ml reactor equipped with an ampoule containing 50 ml of isoprene and 50 ml of n-heptane, and an ampoule containing 2 ml of the initiator solution of Example 5 was prepared. The air inside the system was removed and the reaction system was dried under subatmospheric pressure, thereafter 30 ml of n-heptane purified and degasified in advance, were charged in the reactor. First, by breaking the ampoule, 2 ml of the initiator solution were charged into the reactor, and then at room temperature the seal was broken and the n-heptane solution of the isoprene monomer was mixed with the initiator solution, the mixture was stirred, heated to 60°C. and left to stand for 2 hours. After 2 hours, the reaction product was then added to 1 liter of methanol containing 0.3 g. of antioxidant, β -phenylnaphthylamine to precipitate the polymer. The precipitate was filtered off and dried at 50°C. under subatmospheric pressure for 48 hours. The conversion was 99%.

- 35 Micro structure of the polymer:
- | | |
|----------------------------|--------|
| Cis-1,4 structure | 91% |
| 3,4 structure | 8% |
| 1,2 structure | 1% |
| Molecular weight (average) | 60,000 |
| 40 Q value | 1.50 |

EXAMPLE 7

- 45 A reactor equipped with an ampoule containing 68 ml of isoprene and 100 ml of toluene, and an ampoule containing 2 ml of the initiator solution of Example 5, was prepared. The air inside the system was dried and 50 ml of toluene purified and degasified in advance, were charged to the reactor under subatmospheric pressure. First the initiator solution was introduced into the reactor by breaking the ampoule and then at 25°C. a seal was broken and the toluene solution of isoprene monomer was added to the initiator solution and the mixture was stirred. The mixture was left to stand at 30°C. for 6 hours and, thereafter the reaction product was added to 1 liter of methanol containing 0.2 g of antioxidant, β -phenylnaphthylamine, to precipitate the polymer. The precipitate was filtered off and dried at 50°C. under sub-atmospheric pressure for 48 hours. The conversion was 96.8%.

Microstructure of the polymer:

Cis-1,4 structure	92%	65
3,4-structure	7%	
1,2-structure	1%	
Molecular weight (average)	61,000	
Q value	1.68	

EXAMPLE 8

The following components were polymerized under the conditions of Example 2.

Petroleum ether	200 ml	75
Isoprene	100 ml	
Initiator solution (of Example 5)	5 ml	
Conversion	96.8%	
Cis-1,4 structure	92%	
3,4-structure	6%	
1,2-structure	2%	
Molecular weight (average)	48,000	80
Q value	1.46	

EXAMPLE 9

To 24 ml of the 116 ml of the polymer solution obtained in Example 4, 0.025 mol of methyl methacrylate (MMA) dissolved in 20 ml of tetrahydrofuran was added. When the mixture was left to stand at 25°C. for 18 hours, 65% of the added MMA was copolymerized. The micro structure of the isoprene unit was the same as that of Example 4.

The polymer so produced was a block copolymer of MMA-cis 1,4 polyisoprene-MMA. From this block copolymer, a film was produced by casting. The film was transparent, exhibiting rubber elasticity.

EXAMPLE 10

To 23 ml of the 116 ml of polymer solution obtained in Example 4, 0.12 mole of acrylonitrile dissolved in 20 ml of tetrahydrofuran was added. The reaction was conducted at 10°C. for 20 hours, thereafter the produced polymer was treated by the process of Example 2.

Of the acrylonitrile added, 10%, was block copolymerized. A film prepared from this block copolymer exhibited rubber elasticity.

EXAMPLE 11

By the process of Example 2, polymerization was carried out under an atmosphere of high-purity argon.

Initiator solution (of Example 3)	2 ml	115
Isoprene	0.2 mole	
n-Hexane	50 ml	
Conversion	99.6%	

The polymerization was carried out at 60°C. for 30 minutes and at 30°C. for 20 hours. The polymer obtained was treated by the process of Example 2.

8

5	Conversion	99.6%
	Cis-1,4 structure	93%
	3,4 structure	6%
	1,2 structure	1%
	Molecular weight (average)	3.9×10^3
	Q value	1.98

The amount of each reagent was as follows.

(1)	{ Diphenyl	0.01 mole	60
	{ Lithium	0.04 mole	
	{ Diethylether	100 ml	

A diphenyl-lithium complex compound was synthesized, after separating excess lithium, isoprene was added.

(2)	Isoprene	0.02 mole
(3)	Cyclohexane	4×100 ml

Using the polymer obtained, by the standard rubber compound method described in Example 2, a test piece having the following mechanical properties was prepared.

300% modulus (kg/cm ²)	Tensile strength (kg/cm ²)	Elongation (%)	Hardness (Shore A)
12.5	123	1000	27

The total of 400 ml of cyclohexane was used to carry out the operation for the removal of residual diethylether 4 times. 200 ml of cyclohexane were then added to produce an initiator solution. The alkali metal concentration of the initiator solution was 0.022 mole/liter.

EXAMPLE 12
Polymerization was carried out in vacuo by the process of Example 6.

20	Initiator solution (of Example 3)	5 ml
	Isoprene	0.18 mole
	Benzene	133 ml

The polymerization was carried out at 60°C. for 30 minutes and at 30°C. for 20 hours.

40 ml. was removed from the polymer solution so produced and treated with methanol.

30	Conversion	98.6%
	Cis-1,4 structure	93%
	3,4 structure	6%
	1,2 structure	1%
	Molecular weight (average)	1.37×10^3
	Q value	1.75

EXAMPLE 13
To 40 ml of the 150 ml of polymer solution obtained in Example 12, 0.025 mole of styrene dissolved in 20 ml of tetrahydrofuran was added at 30°C., the mixture was reacted at said temperature for 20 hours, and thereafter it was treated with methanol.

78% of the added styrene had reacted and a block copolymer of styrene-cis 1,4-polyisoprene-styrene was obtained.

The Q value of the obtained block copolymer was 1.70.

From this block copolymer a test piece was prepared by a casting and tests of mechanical properties were conducted. The results were as follows.

50	300% modulus (kg/cm ²)	Tensile strength (kg/cm ²)	Elongation (%)	Hardness (Shore A)
	13.0	105	1300	82

EXAMPLE 14
(preparation of an initiator solution)
An initiator solution was prepared by the process of Example 1.

EXAMPLE 15
A 10-liter pressure-resistant stainless container (reactor) equipped with a stirring rod, an inlet for an initiator solution, an inlet for a cyclohexane solution of isoprene monomer and an entrance for inserting a thermometer was prepared. After the interior of the system had been dried, under an atmosphere of pure N₂, 100 ml of the initiator solution of Example 14 and 600 ml of cyclohexane were charged into the reactor and stirred. After the temperature had been made 5°C., 500 ml of isoprene were added. After the addition, the temperature was kept at 5°C. and stirring was continued for 24 hours. The polymer so produced was then treated in the same way as that of Example 2.

	Conversion	97%	95
	Cis-1,4 structure	94%	
	3,4-structure	6%	
	1,2 structure	trace	
	Molecular weight (average)	360,000	
	Q value	1.75	

The test piece prepared from the polymer was tested for mechanical properties. The mechanical properties of this vulcanized rubber were as follows.

	Tensile strength (kg/cm ²)	126	105
	Elongation (%)	930	
	300% Modulus (kg/cm ²)	12.1	
	Hardness (Shore-A)	27	

EXAMPLE 16
By the process of Example 15, using 100 ml of the initiator solution of Example 14, 410 of butadiene were added at -15°C. in 600 ml of benzene and polymerization was carried out under an atmosphere of high-purity N₂. The butadiene was liquefied by cooling to -15°C collected in a measuring vessel and then added to the reactor.

Tensile strength (kg/cm ²)	97.5
Elongation (%)	1150
300% Modulus (kg/cm ²)	9.0
Hardness (Shore-A)	26

was dissolved in 100 ml of n-heptane and a mixture having an alkali metal concentration of 0.25 mole/liter was prepared. This initiator mixture was a non-uniform slurry, and was used as polymerization initiator for isoprene. The conditions of polymerization were as follows.

- 5 **EXAMPLE 23**
(preparation of an initiator solution)
By the process of Example 1, an initiator solution was prepared.
The amount of each reagent was as follows.

10 (1)	{ Anthracene	0.01 mole
	{ Lithium	0.1 mole
	{ Diethylether	100 ml
(2)	1-Phenylbutadiene	0.02 mole
(3)	Toluene	400 ml

Isoprene	1.06 mole	
n-Heptane	800 mole	
Initiator	1.13×10^{-3} mole	
Reaction temperature	50°C.	65
Reaction time	24 hours	
Conversion	96.5%	

The reaction system at the time of polymerization was non-uniform.

- 15 The total of 400 ml of toluene was used to carry out the operation for the removal of residual diethylether 4 times. Then 200 ml of toluene were added to obtain an initiator solution, the alkali metal concentration of which was 0.028 gm. atom/liter.

Cis-1,4 structure	91.0%	70
Molecular weight (average)	2.77×10^5	
Q value	2.67	

The mechanical properties of a vulcanized rubber of the obtained polymer were as follows.
The compounding was carried out as in Example 2.

25 Toluene	5000 ml
Butadiene	410 ml (-15°C.)
Initiator solution (of Example 23)	50 ml
Conversion	94%
30 1,2 structure	9%
Trans-1,4 structure	49%
Cis-1,4 structure	42%
Molecular weight (average)	410,000
Q value	2.67

300% Modulus (kg/cm ²)	10.0	
Tensile strength (kg/cm ²)	23.0	
Elongation (%)	650	80
Hardness (Shore-A)	26	

- 35 **REFERENTIAL EXAMPLE 1**
(a process corresponding to that of U.S. Patent Specification No. 3,157,604)
A polymerization initiator was prepared by mixing and reacting the following amounts of materials.

Naphthalene	0.01 mole
Lithium	0.5 mole
Isoprene	0.03 mole
Diethylether	100 ml

REFERENTIAL EXAMPLE 2
To 0.01 mol of the initiator slurry obtained by the process of Referential Example 1, 0.05 mol of isoprene was added, but the latter did not dissolve in the former and the resultant mixture which was used as polymerization initiator for isoprene, was non-uniform.

The polymerization conditions were as follows.

The reaction was carried out in vacuo.

- 45 The reaction condition were as follows.

Reaction temperature	25°C.
Reaction time	48 hours

The reaction system at the time of polymerization was non-uniform.

- 50 The reaction was carried out in vacuo, 2 hours after starting the reaction, 0.015 mole of isoprene was added and 2 hours thereafter another 0.015 mole of isoprene was added and the reaction was continued for 44 hours. Diethylether was removed by vacuum distillation. The residual solid

Cis-1,4 structure	89.0%
Molecular weight (average)	2.3×10^5
Q value	2.30

The mechanical properties of a vulcanized rubber prepared from the obtained polymer were as follows.

300% Modulus (kg/cm ²)	7.8
Tensile strength (kg/cm ²)	18.0
Elongation (%)	700
Hardness (Shore-A)	27

5 **REFERENTIAL EXAMPLE 3**
(a process corresponding to that of U.S.
Patent Specification No. 3,170,903)

Naphthalene	0.01 mole
Lithium	0.05 mole
Diethylether	100 ml

15 The above components were charged in a flask equipped with a magnetic stirring device, and the mixture was stirred at 20°C. for 48 hours. Diethylether was removed at 30°C. by distillation in vacuo. Thereafter, n-heptane was added to dissolve the solid component, the mixture was stirred for 1 hour and then n-heptane was removed by distillation thereby completely to remove the ether. Finally, n-heptane was added to the mixture to prepare a 0.035 mole/liter solution of n-heptane, which was used as polymerization initiator for the next polymerization.

20 The reaction was carried out in vacuo under the following conditions.

Isoprene	0.20 mole
n-Heptane	100 ml
Initiator	0.22×10^{-3} mole
Polymerization temperature	30°C.
30 Polymerization time	48 hours
Conversion	89.0%
Cis-1,4 structure	89.0%
Molecular weight (average)	3.8×10^5
Q value	3.28

35 The reaction system of polymerization was non-uniform.

Values of mechanical properties of a vulcanized rubber prepared from the obtained polymer were as follows.

40 300% modulus (kg/cm ²)	7.4
Elongation (%)	620
Tensile strength (kg/cm ²)	16
Hardness (Shore-A)	27

45 **REFERENTIAL EXAMPLE 4**
An example of the preparation of a block copolymer using the polymerization initiator of Referential Example 1 will be shown.

The reaction was carried out in vacuo under the following conditions.

50 Isoprene	0.25 mole
Benzene	100 ml
Initiation (prepared in Referential Example 1)	0.30×10^{-3} mole
Polymerization temperature	30°C.
55 Polymerization time	48 hours

After the completion of polymerization of

isoprene (a part of the system was taken and 100% of conversion was confirmed), 50 ml of tetrahydrofuran were added and the mixture was well stirred. At that time insoluble material was dissolved and the system became uniform.

Next 0.052 mole of styrene dissolved in 20 ml of tetrahydrofuran (THF) was added. The copolymerization was carried out under the following conditions.

Polymerization temperature	10°C.
Polymerization time	24 hours

The polymerization system was a uniform solution, conversion was 98.3% and Q value was 3.06.

The obtained polymer was dissolved in toluene and a film was made by casting. This film was opaque, and did not have any rubber elasticity.

REFERENTIAL EXAMPLE 5
(incomplete removal of the polar (i.e. ether) solvent)
Preparation of an initiator solution)

Naphthalene	0.10 mole
Metallic lithium	0.12 mole
Diethylether	100 ml

The aforementioned components were charged in a flask having a stirrer under an atmosphere of nitrogen, and the mixture was stirred at room temperature of 23°C. for 4 hours. The interior of the system was kept under an atmosphere of purified nitrogen. Next, 0.020 mole of isoprene was added, and the mixture was stirred for 1 hour, next 130 ml of n-heptane, purified in advance, were added, the reaction solution was stirred with heating and diethylether was removed by distillation. As soon as diethylether stopped distilling off, heating and distillation were immediately stopped, and the mixture was placed under nitrogen pressure and retained. The alkali metal concentration of the initiator solution was 0.74 gm-atom/liter. The amount of diethylether in the initiator solution was 1.5% by weight.

Using the initiator solution obtained by the foregoing reaction, polymerization of isoprene was carried out. The polymerization reaction used the following device. Namely, it was a flask equipped with a magnetic stirrer, heated and dried in advance and the air inside the flask was replaced by nitrogen in advance.

Said flask was charged with 100 ml of purified petroleum ether and 20 ml of isoprene, and while the mixture was stirred, 10 ml of an initiator solution were added thereto. The reaction temperature was 25°C. and the reaction time was 4 hours.

The polymer so produced was treated with methanol. The amount of diethylether exist-

ing in the reaction system was 0.007 mole per mole of isoprene and the conversion was 91%.

The micro structure of the obtained polymer was as follows.

3,4-structure	26%
1,2-structure	4%
Cis-1,4 structure	70%
Molecular weight (average)	39,000
Q value	1.86

REFERENTIAL EXAMPLE 6

(non-removal of metallic lithium)

In the preparation of an initiator solution by the process of Example 1, an initiator solution was prepared without filtering off unreacted excess metallic lithium. The amount of each reagent was as follows.

(1)	{	Napthalene	0.01 mole
		Lithium	0.5 mole
		Diethylether	100 ml

Thus the diethylether solution of the naphthalene-lithium complex compound, contained metallic lithium because the lithium had not been filtered off. 0.03 mol of purified styrene monomer was added in vacuo to the solution and, the reaction was carried out as in Example 1. 300 ml of benzene were used to remove the diethylether as in Example 1 and then 100 ml of benzene were added to produce an initiator mixture. However, this mixture was in the form of a slurry.

The amount of ether in this initiator slurry was less than 0.01% by weight and the alkali metal concentration of this slurry was 0.185 gm-atoms/liter.

The polymerization of isoprene was carried out in high-purity N₂ using this initiator by the process of Example 2.

Initiator solution	8 ml
Isoprene	200 ml
Benzene	400 ml

The results were as follows.

Conversion	94%
Cis-1,4 structure	89%
3,4 structure	10%
1,2 structure	1%
Molecular weight (average)	260,000
Q value	3.67

Mechanical properties of a vulcanized rubber prepared using the polymer obtained in the aforementioned process were as follows.

Tensile strength (kg/cm ²)	19
Elongation (%)	730
300% Modulus (kg/cm ²)	8.3
Hardness (Shore-A)	25

WHAT WE CLAIM IS:—

1. A process for preparing a lithium-hydrocarbon adduct which process comprises (i) reacting, in the presence, as solvent, of an aliphatic ether, metallic lithium with a polycyclic aromatic hydrocarbon having 10 to 30 carbon atoms; (ii) removing insoluble material from the reaction product of (i); (iii) adding to the solution obtained from (ii) 1 to 10 moles per gram-atom of lithium in the solution of a conjugated diene hydrocarbon or a vinyl- or vinylidene-substituted aromatic hydrocarbon; and then (iv) substantially removing all the aliphatic ether from the resulting solution.

2. A process according to claim 1 wherein the polycyclic aromatic hydrocarbon is naphthalene, anthracene, phenanthrene or diphenyl.

3. A process according to claim 1 or 2 wherein the aliphatic ether is diethyl ether or tetrahydrofuran.

4. A process according to any one of claims 1 to 3 wherein the conjugated diene hydrocarbon or vinyl- or vinylidene-substituted aromatic hydrocarbon is styrene, isoprene, α -methylstyrene or 1-phenylbutadiene.

5. A process according to claim 1 substantially as described in any one of Examples 1, 3, 5, 14, 19, 21 and 23.

6. A lithium-hydrocarbon adduct prepared by the process claimed in any one of the preceding claims.

7. A process for polymerising a conjugated diene which comprises polymerising an anion-polymerisable conjugated diene hydrocarbon in a non-polar solvent in the presence of a lithium-hydrocarbon adduct claimed in claim 6.

8. A process according to claim 7 wherein there is formed a block copolymer by polymerising alternately (a) an anion-polymerisable conjugated diene in non-polar solvent in the presence of the lithium-hydrocarbon adduct and (b) an anion-polymerisable monoethylenically unsaturated monomer; the amount of monoethylenically unsaturated monomer (b) being such as to provide less than 50% by weight of units derived from (b) in the final polymer.

9. A process according to claim 8 wherein the anion-polymerisable monoethylenically unsaturated monomer (b) is styrene, α -methylstyrene or vinyl toluene.

10. A process according to claim 7 wherein there is formed a block copolymer by first polymerising an anion-polymerisable conjugated diene in a non-polar solvent in the presence of the lithium-hydrocarbon adduct and then polymerising an anion-polymerisable monoethylenically unsaturated monomer in the presence of the polymer chain so formed; the amount of monoethylenically unsaturated monomer being such as to provide less than

50% by weight of units derived therefrom in the final polymer.

5 11. A process according to claim 10 wherein the anion-polymerisable monoethylenically unsaturated monomer is styrene, α -methyl styrene, vinyl toluene, vinyl xylene, ethyl vinyl benzene, methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate, acrylonitrile or methacrylonitrile.

10 12. A process according to any one of claims 7 to 11 wherein the anion-polymerisable conjugated diene hydrocarbon is isoprene or butadiene.

13. A process according to claim 7 substantially as described in any one of Examples 2, 4, 6 to 13, 15, 16, 17, 18, 20, 22 and 24. 15

14. Conjugated diene polymers prepared by the process claimed in any one of claims 7 to 13. 20

J. A. KEMP & CO.,
Chartered Patent Agents,
14, South Square,
Gray's Inn,
London, WC1R 5EU.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1971.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.